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PEPTIDE-ASSEMBLED OPTICALLY RESPONSIVE NANOPARTICLE COMPLEXES

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14. ABSTRACT

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Peptide-Assembled Optically Responsive Nanoparticle Complexes

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ABSTRACT

The design of active nanostructures whose form and properties can be modulated by remote means is an important challenge in nanoscience. Here we report two types of active nanoparticle complexes, with properties controlled by near-infrared illumination, resulting from the assembly of photothermally responsive plasmonic nanoparticles with thermally labile biomolecular linkers. Au nanoshells (NS) and quantum dots (QD) are assembled using coiled-coil peptides into NS−NS and NS−QD complexes. Illumination of the NS−NS complexes results in reversible disassembly reassembly, while illumination of NS−QD complexes results in a large, reproducible modulation of the quantum dot fluorescence without disassembly of the nanoparticle−peptide complex.

The biological assembly of nanoparticles has led to advances in device fabrication, photonics, catalysis,[1,2] electronics,[3−5] and sensor development[6−9] as a result of the precise control that biological systems offer. For example, Au nanoparticles have been assembled into discrete networks using DNA hybridization[10,11] and various peptide motifs.[12−15] Bimetallic catalytic particles have been prepared by peptide-templated synthesis,[16,17] while microorganisms[4] and viruses[3] have been used to organize gold nanoparticles into conductive networks. In addition to directing assembly, the dynamic nature of biomolecules has also been exploited to induce structural changes in nanoparticle complexes under certain controlled conditions. For example, the release of encapsulated CdS particles by the heat shock protein GroEL can be triggered by addition of ATP.[18] Conformational changes to biomolecules can be stimulated by various environmental conditions, such as temperature, pH, solvent, and ionic concentration.[19] In living systems, these changes are often used to signal biochemical events and pathways; in abiotic systems, they present useful mechanisms for the external triggering of structural changes in nanoparticle assemblies or networks.[19] For example, pH modulation has been shown to promote the disassembly of a coiled-coil leucine zipper peptide based gold nanoparticle structure[13,15] and DNA-functionalized gold nanoparticle assemblies.[11]

Plasmonic nanoparticles, metal-based nanoparticles whose optical resonant properties are controlled by their geometry,[20,21] are highly promising components for imparting optical responsivity into nanoscale structures. This useful class of nanoparticles combines structurally tunable optical properties with facile conjugation of biomolecules to their surfaces. Optically, nanoshells can be designed to scatter and/or absorb light over a broad spectral range. Their large absorption cross-section combined with their extremely weak fluorescent properties result in a very strong photothermal response upon resonant optical illumination. The large photothermal response of nanoshells has been successfully exploited in numerous actuating applications such as optically triggered drug delivery,[22,23] independently optically addressable materials,[24,25] microfluidic valves,[26] photothermal deletion of cancer cells,[27] and photothermally induced remission of cancerous tumors.[28] These photothermal properties have additional potential in applications such as destruction of biological warfare agents, decontamination of pollutants, or photothermally driven devices and switches, where optical illumination may be used to toggle between a cooled or heated state.

Here we report the use of a coiled-coil peptide motif to assemble two types of active nanoparticle complexes designed to respond specifically to near-infrared resonant light illumination. Extended nanoshell−nanoshell (NS−NS) and discrete nanoshell−semiconductor quantum dot (NS−QD) complexes are assembled using this peptide as a thermally labile interparticle linker. Because Au nanoshells possess a large photothermal response, when they are assembled into

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complexes via this thermally sensitive molecular linker, the structures and properties of the resultant nanoparticle complexes can be modulated remotely using near-infrared illumination. Although the structure, properties, and active modulation response of the NS−NS and NS−QD complexes are quite different, the use of coiled-coil peptides for assembly in both cases results in optically modulated properties that are robust and reversible, capable of being optically cycled numerous times.

Au nanoshells (NS) with plasmon resonances at 805 nm were synthesized as described previously.[29,30] Nanoshells (200 μL, 1.1 × 10^{10} particles/mL) were transferred into 0.1 M phosphate buffer pH 9.0 for subsequent peptide binding. One of the two matching antiparallel coil peptides (E5) −CGGEVSALEKEVSALEKEVSALEKEVSALEKEVSALEK− or (K5) −CGGKVSALKEKVSALKEKVSALKEKVSALKEKVSALKE−[31] (3 μL, 10 mg/mL, New England Peptide Inc.) were then added to the nanoshell suspensions and incubated for 2 h. Unbound peptide was then removed through three cycles of centrifugation and dialysis in deionized water. The peptides were conjugated to the nanoshells through Au−thiol binding. FT-IR spectroscopy, obtained on a Perkin-Elmer FT-IR spectrometer SPECTRUM 2000 with AutoImage system, was used to confirm the presence of NS-bound coil peptide, through the absence of S−H stretching modes and the appearance of amide I and II vibration modes.

Purified E5 and K5 peptide-functionalized NS components were incubated together for 2 h, resulting in nanoshell complexes that were assembled orthogonally at a 1:1 ratio via a coiled-coil formation. The assembled NS−NS structures were characterized using a CPS disk centrifuge particle size analyzer DC240000 and using a Phillips CM200 transmission electron microscope (TEM) (Figure 1). Free-peptide-functionalized Au nanoshells showed a bimodal size distribution with a diameter of 122 ± 15 nm for the major fraction similar to the unfunctionalized nanoshells (Figure 1B); nanoshells assembled with complementary coil peptides exhibited a size of 205 ± 60 nm, indicative of dimers (Figure 1C). Consistent with the particle size analysis data, TEM micrographs of the assembled nanoshell complexes show the predominance of large nanoshell aggregates relative to free nanoshells.

The peptide-assembled structures possessed excellent stability against external heating and chemical denaturants. This property is entirely due to the stability of the coiled-coil peptide complex to heat (T_m > 85 °C) and to guanidinium HCl, thereby making the NS−NS structures resilient to conventional biochemical methods used for protein denaturation. However, it is possible to trigger the disassembly of these nanoshell complexes by utilizing the intrinsic photothermal properties of nanoshells. Near-IR illumination was achieved with a 810 nm molded 3× LEDs (Marubeni Corp, 20 mW). The NS−NS structures were irradiated for 15 min with 808 nm incident light, well within the line width of the plasmon resonance,[32] to induce temperature-mediated unfolding of the coiled-coil peptide interface and therefore promote disassembly. As a result, the nanoparticle−peptide complexes were nearly completely disassembled into the

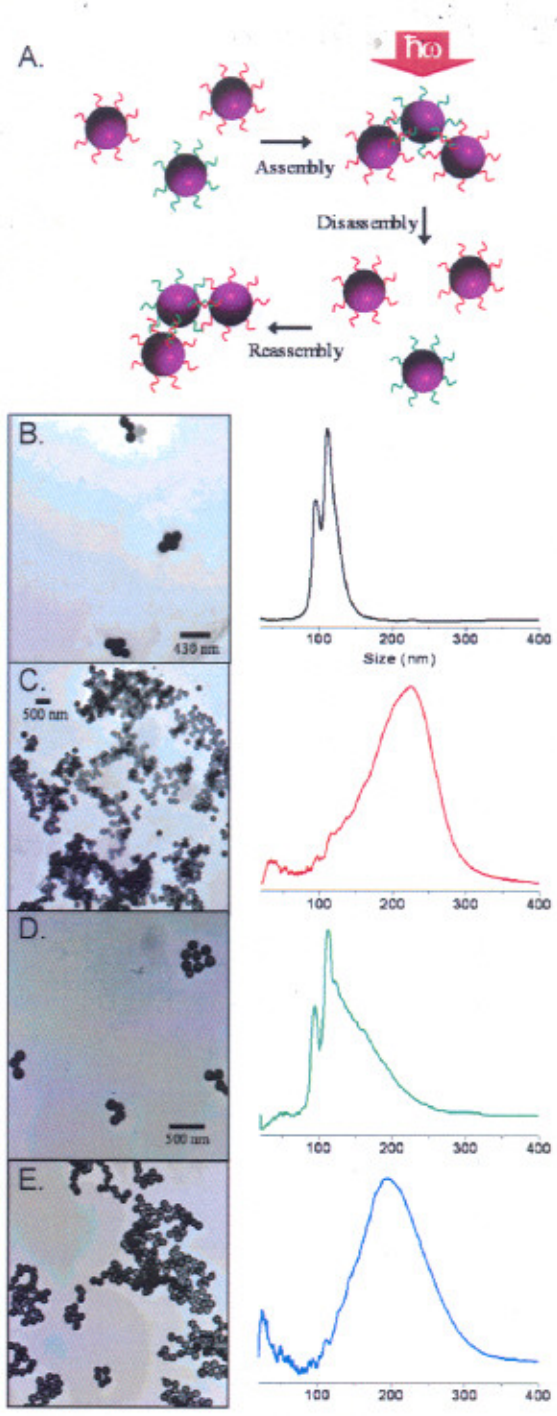

Figure 1. Assembly and disassembly of coiled-coil peptide functionalized nanoshell complexes. (A) Schematic illustration of the light-induced assembly/disassembly process. TEM micrographs (left panels) CPS particle size analysis (right panels) of (B) free nanoshell functionalized with E5 coil peptide, (C) assembled NS−NS complexes, (D) near-IR disassembled structures, and (E) reassembled nanoshell complexes following irradiation.

individual NS components as observed by the lack of the larger aggregates by TEM (Figure 1D). In addition, the particle size analysis of the irradiated structure revealed a size distribution centered around 122 ± 39 nm, consistent with disassembled free nanoshells. The tail of the CPS plot indicates that a small number of residual dimer particles

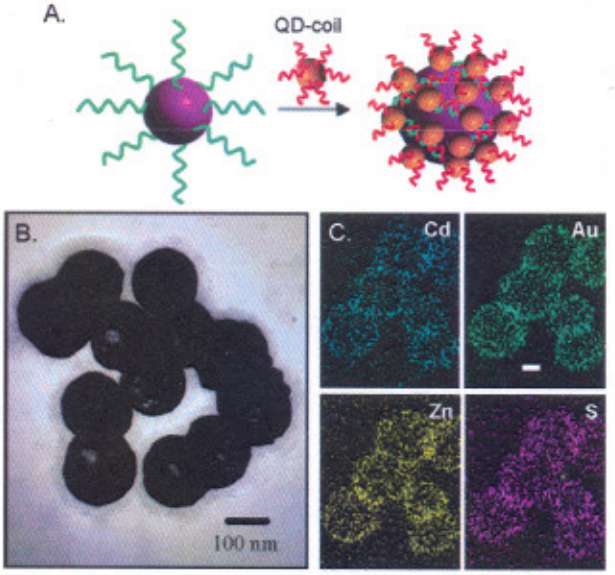

Figure 2. Assembly and characterization of NS−QD structures. (A) Schematic of the assembly process. (B) TEM image of NS−QDs. (C) EDAX maps for Au, S, Zn, and Cd on the NS−QD complexes. Scale bar, 90 nm.

persisted. Notably, this externally triggered disassembly was found to be reversible. Five minutes after irradiation had ceased, the coil-functionalized nanoshells reassembled to form the original NS−NS coiled-coil structure (Figure 1E) due to reversible folding of the peptides upon cooling.

In the case of the peptide-assembled NS-QD heterocomplexes, discrete nanoparticle assemblies were obtained consisting of individual peptide-conjugated nanoshells linked to multiple QDs at their surfaces (Figure 2). Similar to the NS−NS complexes, nanoshells and quantum dots were functionalized with matching antiparallel coil peptides, E5 and K5, respectively. CdSe/ZnS Evitag−Fort Orange−Carboxyl quantum dots (QD) (Evident Technologies, catalog no. ET-C11-CB1-0600, conc 0.25 mg/mL) were functionalized with coil K5 peptide through disulfide linkage between the N-terminal cysteine residue of K5 and the cysteine-modified QDs by incubating 3 μL of coil peptide K5 with 50 μL of QD−COOH that had been activated with 20 μL of EDC/NHS and 50 μL of 0.1 M cysteine. TEM analysis revealed several uniform layers of quantum dots on the nanoshell surface (Figure 2B) with characteristic lattice fringes for the QDs. EDAX mapping of the NS−QD structure confirmed the association of the Cd, Zn, and S of the quantum dot with the Au of the nanoshell (Figure 2C). In contrast, substitution of a coil peptide with a random peptide sequence (−DYKDDDDKPAYSSGAPPMPPF−) on the quantum dots resulted in no formation of NS−QD structures.

The peptide-assembled NS−QD heterostructure complexes give rise to a dramatic active response upon illumination (Figure 3). Because metal nanoparticles significantly alter the emission of nearby fluorophores,[33,34] the fluorescence from the NS−QD structures was monitored during assembly using a Varian Cary Eclipse fluorimeter. Initially, as the NS−QD complexes assemble (prior to illumination), the QDs are

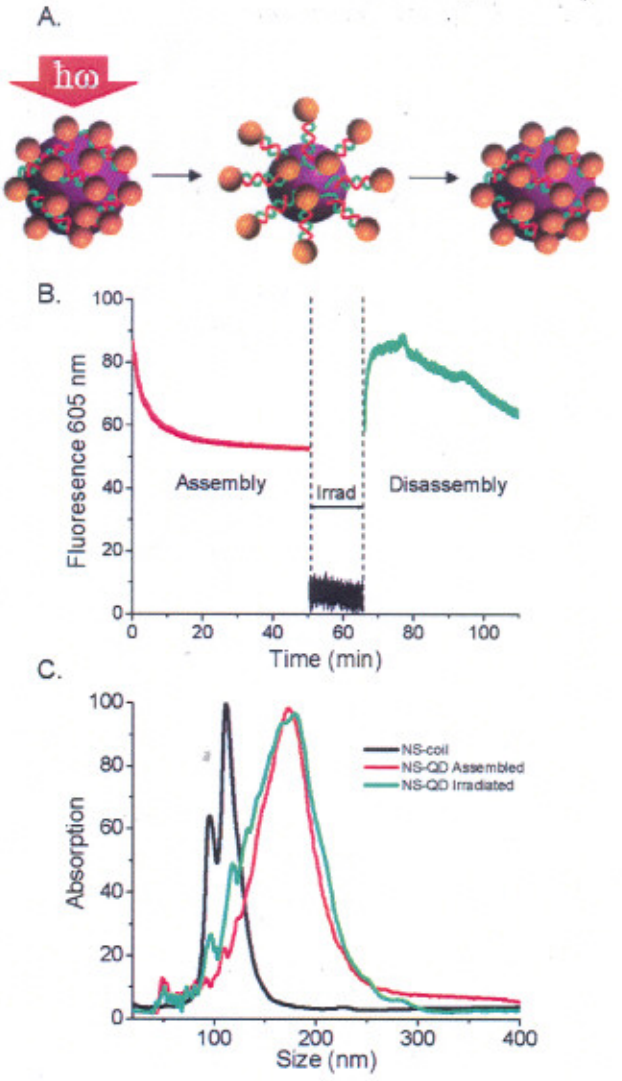

Figure 3. Near-IR irradiation of NS−QD structures. (A) Schematic of the assembly process. (B) Time plot of fluorescence at 605 nm during assembly and after irradiation. Fluorescence measurements were collected and averaged every 5 s for the assembly process; measurements were collected continuously following illumination. (C) CPS size plot showing free nanoshells, NS−QD coil assemblies, and irradiated structures.

brought into close enough proximity to the NS surface to result in a quenching of the QD fluorescence at 605 nm to 69% of the free QD emission (Figure 3B). When the NS−QD complexes were irradiated with 808 nm light (using the fluorimeter), a dramatic increase in fluorescence to preassembly levels occurred. This behavior is reminiscent of previously reported fluorescence changes in CdTe−PEG−Au superstructures in response to bulk solution heating.[35,36] Following the dramatic increase in illumination-induced fluorescence, the fluorescence emission of the NS−QD complex then slowly decays back to its initial preillumination value.

Our interpretation of the active response of this heterostructure complex is based on the distance-dependent fluorescence quenching and enhancement of fluorophores by metallic nanoparticles. Because of the partial quenching of

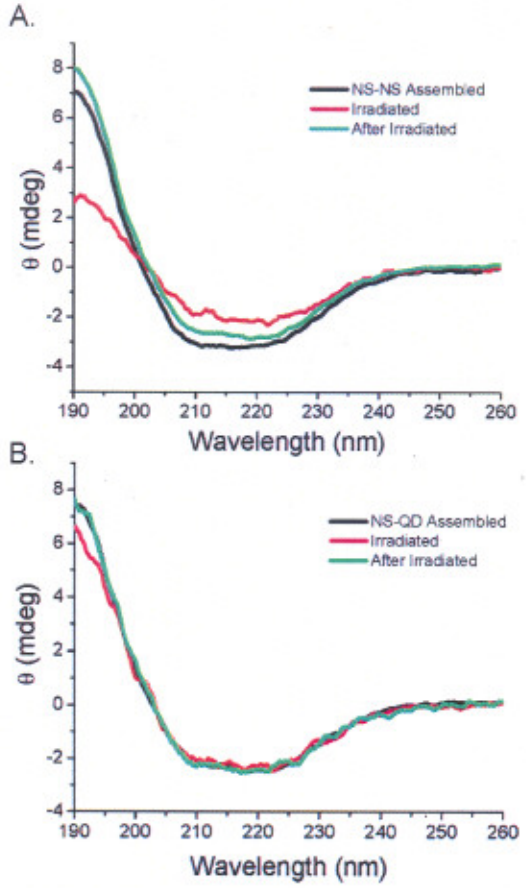

Figure 4. Circular dichroism measurements of (A) NS−NS and (B) NS−QD complexes before and after irradiation.

the fluorescence during initial assembly, it appears that the QDs are located relatively close to the NS surface in equilibrium. Because the fluorescence increases upon illumination, it is likely that this corresponds to an increase in NS−QD distance, either due to a stretching/expansion of the peptide ligands or due to dissociation of the complex. Unlike the NS−NS structures, however, particle size analysis (Figure 3C), gel electrophoresis, and TEM revealed that the NS−QD complexes do not disassemble appreciably upon near-IR illumination. The slow time scale of the observed postillumination fluorescence decay may possibly be due to charging effects upon illumination of the complex: if the QD-ligands become charged, the resulting electrostatic repulsion would inhibit their relaxation back to the nanoshell surface.

Circular dichroism (CD) spectroscopy confirmed that the observed disassembly reassembly of the NS−NS complexes was indeed induced by a change in the secondary structure of the coiled-coil peptides (Figure 4A). In contrast, CD spectroscopy of the NS−QD complexes revealed no such structural change, further supporting the conclusion that the fluorescence modulation in these complexes is not due to disassembly (Figure 4B). Using a Jasco J-720 spectropolarimeter, we monitored the change in secondary structure of the coiled-coil peptides in the NS−NS assemblies in situ with an array of 810 nm LEDs. Upon illumination, the spectrum of NS−NS showed a 30% loss in helicity of the peptide functionalized NSs at θ_{222} and featured a decreased peak at 190 nm attributed to $\pi \rightarrow \pi_{\perp}^{*}$ transition. The change in secondary structure indicates thermal unfolding of the peptide induced by NS photothermal heating and is consistent with the dissociation of other coil peptides.[13] Following illumination, the disassembled coil−NS components regained ~90% of their original helicity upon reassembly of the NS−NS structures. In contrast, there was no difference between the CD spectra of the pre-illuminated and postilluminated NS−QD complexes, indicating no detectable change in the structure of the peptide linkages in this case.

The difference in disassembly between the irradiated NS−NS and NS−QD structures may be due to interactions between the plasmons on adjacent NSs in the NS−NS complexes, which upon irradiation may lead to increased fields in the junction between the nanoparticles, resulting in a greater photothermal dissociative response. In addition, it is likely that heat dissipated more quickly from the relatively isolated nanoshells in the NS−QD structures as opposed to the dense network of the NS−NS complexes.

The ability to control the nanoparticle assemblies remotely by optical illumination has highly valuable potential for ultimately manipulating material properties. We have shown that the coiled-coil peptide assembly of nanoshell−nanoshell and nanoshell−quantum dot complexes results in active nanostructures with light-inducible responses. This method affords a new means to manipulate both structural properties, such as reversible disassembly, as well as optical properties such as fluorescence quenching, without disassembly. In addition, it may be possible to tailor the optical threshold and response kinetics of such optically active nanostructure complexes by modifying the melting transition of the biomolecule interface, a property controlled by the structure of the biomolecules themselves.

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